

Cluster Formation versus Isolated-Site Adsorption. A Study of Mn(II) and Mg(II) Adsorption on Boehmite and Goethite

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The experiments measured the extent of adsorption of Mn(II) and Mg(II) on goethite [α -FeOOH] and boehmite [γ -AlOOH] from pH \cong 4 to pH \cong 11 and the resulting changes in surface charge. The electron spin resonance spectra for the Mn(II)/AlOOH system to monitor changes in the local environment of Mn(II), were also measured as adsorption occurred. The results indicate that Mg(II) adsorbs at relatively few, isolated sites on the goethite surface. When Mn(II) adsorbs on boehmite it forms magnetically ordered arrays, which are referred to as surface "clusters." On the basis of the negligible effect of adsorption on surface charge, it was concluded that there is a high probability of "cluster" formation when Mn(II) adsorbs on goethite and Mg(II) adsorbs on boehmite. The mechanism of adsorption and the tendency to either form "clusters" or adsorb at isolated sites is strongly dependent on the nature of the oxide surface. © 1985 Academic Press, Inc.

INTRODUCTION

Our knowledge and understanding of Mg(II) and Mn(II) adsorption onto oxide surfaces remains rather limited even though adsorption has been studied for a variety of surfaces and under a range of conditions. For a given oxide we know approximately the pH at which adsorption of these ions begins and the pH range within which adsorption occurs (1–3). Adsorption of Mg(II) and Mn(II) begins below the isoelectric point (IEP)¹ for many of the surfaces studied (3–5). From this we can conclude that adsorption of these ions is not a simple ion-exchange reaction with diffuse double-layer ions.

James and Healy (6) have proposed a theory to explain the general relation, observed in many cases, between the pH at which adsorption of a metal ion begins and pK_1 for the hydrolysis of the ion. Their

theory was designed to account for contributions arising from the oxide surface, the solution, and the adsorbing metal ion to the free-energy change on adsorption. Other theories focus primarily on the thermodynamics of site binding (7–10).

Electron spin resonance (ESR) has been used to study Mn(II) adsorption on a variety of surfaces (11–15). The broad ESR signal ($\Delta H = 200$ –230 G) observed by McBride (12) was attributed to manganese(II) carbonate precipitated on a calcium carbonate surface. Hronsky *et al.* (11) observed a broad signal ($\Delta H = 320$ G) for Mn(II) on silica gel and suggested it was due to hydrous Mn(II) clusters in the pores of the gel. Burlamacchi and Martini (14) and Martini (15) did not observe the broad signal reported by Hronsky *et al.* (11) in their studies of Mn(II) on silica gel. They attributed their six-peak signal to hexaquomanganese(2+) loosely bonded to the silica surface. Hronsky and Rakos (13) also reported spectra of Mn(II) on alumina in which a six-peak signal appears. This was attributed to the composite spectra of hexa-

¹ We will follow the convention used by Parks (5) and refer to "the ZPC (zero point of charge) arising from the interaction of H^+ , OH^- , the solid and water alone" as the IEP.

quomanganese(2+) hydrogen bonded to the surface of the alumina via two different arrangements.

Burlamacchi and Martini (14) point out that Mn(II) tightly bonded to the surface would give a very broad, unobservable signal because the zero-field splitting term in the spin Hamiltonian would be quite large. Hydrolysis could also broaden or extinguish the Mn(II) signal even if the cation was loosely bonded to the surface since unsymmetric ion pairs involving Mn(II) show this tendency (16).

Our objective in the research reported herein was to collect data on oxide suspensions containing Mg(II) and Mn(II) in order to clarify the mode of adsorption under a variety of pH conditions. We worked with suspensions containing the same amount of mineral surface area to allow comparison of different surfaces under similar conditions. We chose to compare the adsorption behavior of two ions whose pK_1 for hydrolysis and pK_{so} for hydroxide solubility were similar to see how similar their adsorption characteristics might be.

MATERIALS

We synthesized goethite following the technique outlined by Atkinson *et al.* (17) using 0.1 *M* ferric perchlorate (OH:Fe = 1) and boehmite according to the procedure of Bugosh (18) using aluminum perchlorate. The oxides were washed repeatedly with distilled, deionized water until the pH ceased to decline and then freeze-dried. We measured the specific surface areas by the BET method with N_2 as the adsorbing gas. The surface areas were 82.0 and 41.2 $m^2 g^{-1}$ for goethite and boehmite, respectively.

METHODS

Prepare a stock suspension which contains 150 $m^2 liter^{-1}$ oxide in distilled, deionized water, sonifying to disperse the particles. Pipet into a 125-ml Erlenmeyer flask: 10 ml stock suspension, sufficient $NaClO_4$ stock

solution to give $9.04 \times 10^{-3} M NaClO_4$ when the volume is made up to 75 ml, standardized $HClO_4$ or $NaOH$ solution to adjust the suspension to the desired pH, and sufficient distilled, deionized water to make the final volume 75 ml. Rapidly bring the suspension to a rolling boil and quickly cool in ice water to room temperature. Perform boiling and cooling under oxygen-free argon using the technique described by Bryant (19) and due to Hungate (20). All subsequent manipulations involving suspension preparation, sampling for analysis, and analysis itself are performed under oxygen-free argon using purged containers, syringes, etc.

Once the oxygen-free suspension has cooled to room temperature, inject stock solution of the divalent metal as the perchlorate and stopper the flask with a rubber stopper. It is best to use a sufficiently concentrated stock solution of the divalent metal so that microliter amounts can be added to the suspension, thereby minimizing the introduction of oxygen in this step.

After 24 hr measure the suspension pH. Transfer with a syringe a 15-ml sample of the suspension to a centrifuge tube, stopper and centrifuge until the supernatant is free of suspended particles. Filter the supernatant through a 0.45- μm Metrical membrane filter (Gelman) held in a filter holder mounted at the end of a syringe. If the solution contains manganese, add a known amount of $HClO_4$ to the receptacle to which it is transferred to acidify the sample and prevent oxidation of manganese in solution. Analyze the filtered solution for either magnesium or manganese by atomic adsorption spectroscopy.

We measured the electrophoretic mobility (EM) of the suspension particles using the Riddick Zeta Meter. The mobility of at least 10 particles was measured for each sample, the reported EM representing the mean of these observations.

If ESR spectra are to be taken for metals adsorbed on the oxide, draw a sample of the oxide particles at the bottom of the centrifuge tube mentioned above into a 0.4-mm open-

ended capillary with a syringe. Place the sample-containing capillary inside a 1.5-mm capillary (previously sealed at one end) and seal the other end with a flame to keep the sample free of oxygen until analysis. We did our ESR analyses using a Varian E-104 spectrometer.

The surface area in all suspensions was $20 \text{ m}^2 \text{ liter}^{-1}$. Taking the hydrated radius of the divalent ions to be $3.42 \times 10^{-10} \text{ m}$, complete adsorption of $9.04 \times 10^{-5} \text{ M}$ Mg(II) or Mn(II) by an oxide suspension with $20 \text{ m}^2 \text{ liter}^{-1}$ surface area would, at most, cover the surface with a close-packed monolayer of hydrated ions. We use this concentration, or multiples of it, as a means of relating the amount adsorbed to the *potential* coverage of the surface. We do not imply that once the ions are adsorbed they necessarily cover the surface as close-packed hydrated ions.

RESULTS

The electrophoretic mobility (EM) of boehmite and goethite suspensions over a

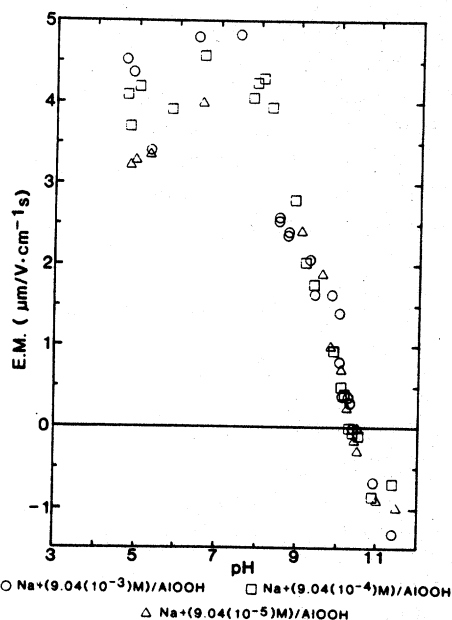


FIG. 1. The electrophoretic mobility of boehmite particles ($20 \text{ m}^2 \text{ liter}^{-1}$) as a function of pH, in three concentrations of NaClO_4 : 9.04×10^{-5} , 9.04×10^{-4} , and $9.04 \times 10^{-3} \text{ M}$.

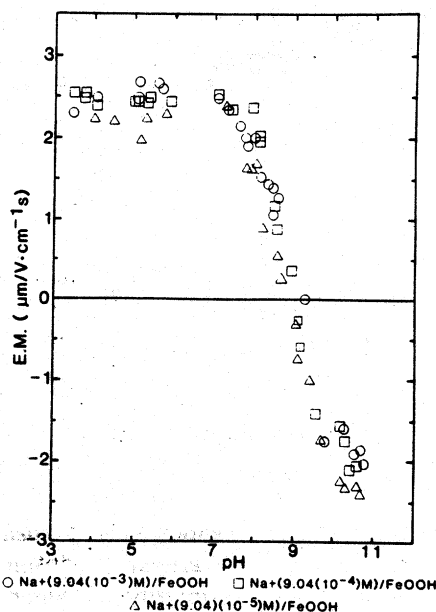


FIG. 2. The electrophoretic mobility of goethite particles ($20 \text{ m}^2 \text{ liter}^{-1}$) as a function of pH, in three concentrations of NaClO_4 : 9.04×10^{-5} , 9.04×10^{-4} , and $9.04 \times 10^{-3} \text{ M}$.

range of pH and in three different salt solutions are shown in Figs. 1 and 2. The pH of zero particle mobility, which we refer to as the isoelectric point (IEP), is 9.0 ± 0.2 and 10.4 ± 0.1 for goethite and boehmite, respectively. In all adsorption experiments we used $9.04 \times 10^{-3} \text{ M}$ NaClO_4 as the background electrolyte. The ionic strength of the solutions and the particle size of the oxides for these experiments satisfy the Helmholtz-Smoluchowski limiting conditions (21). The zeta potentials at low pH, determined using the Helmholtz-Smoluchowski formula, are 34 and 54 mV for goethite and boehmite, respectively. The boehmite carries about 50% more surface charge per unit area than the goethite based on calculated zeta potentials.

Figures 3a and b show EM and adsorption experiment results for goethite suspensions containing Mg(II). As mentioned earlier the initial concentrations correspond to sufficient Mg(II) in solution to cover the surface, on complete adsorption from solution, with close-packed hydrated ions one, two and four

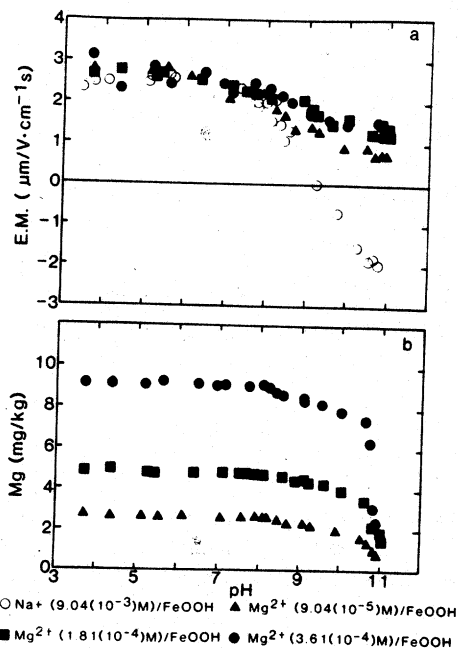


FIG. 3. The variation of the (a) electrophoretic mobility of suspension particles and (b) solution concentration of $\text{Mg}(\text{II})$ as a function of pH, for goethite suspensions ($20 \text{ m}^2 \text{ liter}^{-1}$) in $9.04 \times 10^{-3} \text{ M}$ NaClO_4 and three initial concentrations of $\text{Mg}(\text{ClO}_4)_2$: 9.04×10^{-5} , 1.81×10^{-4} , and $3.61 \times 10^{-4} \text{ M}$.

layers thick. Adsorption of $\text{Mg}(\text{II})$ begins at about pH 7.6–7.9, below the IEP of goethite. At the IEP the surface coverage ranges from 10 to 25%, depending on the initial $\text{Mg}(\text{II})$ concentration. Only a small percentage of the surface need be covered in order to

prevent charge reversal at the IEP. The rapid decrease in solution $\text{Mg}(\text{II})$ at pH values above 10.6 is due to the precipitation of $\text{Mg}(\text{OH})_2(\text{s})$ rather than adsorption (Fig. 4a). At the pH where the solubility of the hydroxide is exceeded, potential surface coverage is at most 50% of a monolayer.

By contrast, boehmite suspensions containing $\text{Mg}(\text{II})$ behave quite differently (Figs. 5a and b). Adsorption of $\text{Mg}(\text{II})$ begins at a pH between 7.5 and 8.5, below the IEP of boehmite. At the IEP adsorption of $\text{Mg}(\text{II})$ from solution is complete for all initial concentrations. In fact, if we consider the highest initial concentration of $\text{Mg}(\text{II})$, full adsorption is sufficient to cover the surface uniformly with close-packed hydrated ions four layers thick. At any given pH above 9, the particles in the boehmite suspension containing $\text{Mg}(\text{II})$ have a lower EM than those in the $\text{Mg}(\text{II})$ -containing goethite suspension even though much more $\text{Mg}(\text{II})$ has been adsorbed in the former suspensions. At no point is the solubility of $\text{Mg}(\text{OH})_2(\text{s})$ exceeded in the boehmite suspensions (Fig. 4b).

The adsorption behavior of $\text{Mn}(\text{II})$ on goethite is quite different from $\text{Mg}(\text{II})$ on the same surface (Figs. 6a and b). Adsorption of $\text{Mn}(\text{II})$ begins in the pH range 6.0 to 6.5, much lower than for $\text{Mg}(\text{II})$, and is essentially complete at the IEP. The solubility of the hydroxide is never exceeded, even when large amounts of $\text{Mn}(\text{II})$ have been adsorbed. The

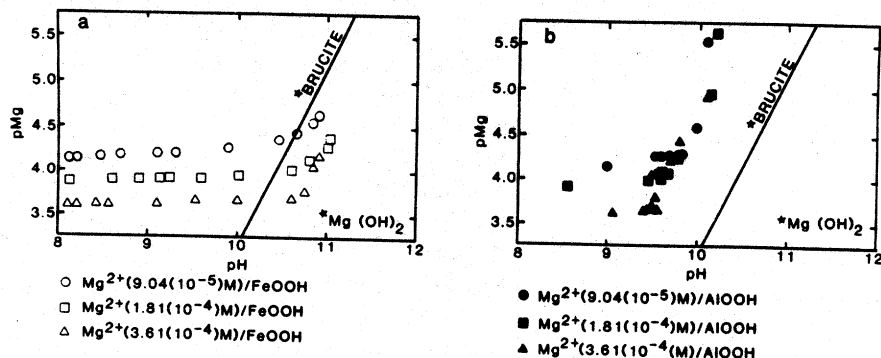


FIG. 4. Diagrams showing the variation of pMg as a function of pH for (a) goethite suspensions of Fig. 3 and (b) boehmite suspensions of Fig. 5.

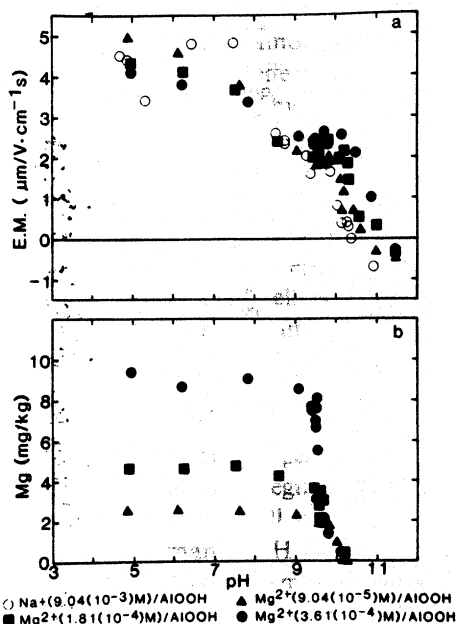


FIG. 5. The variation of the (a) electrophoretic mobility of suspension particles and (b) solution concentration of Mg(II) as a function of pH, for boehmite suspensions ($20 \text{ m}^2 \text{ liter}^{-1}$) in $9.04 \times 10^{-3} \text{ M}$ NaClO₄ and three initial concentrations of Mg(ClO₄)₂: 9.04×10^{-3} , 1.81×10^{-4} , and $3.61 \times 10^{-4} \text{ M}$.

effect of the adsorbed Mn(II) on the EM of the particles is negligible.

Results for EM and adsorption experiments of boehmite suspensions containing Mn(II) are shown in Figs. 7a and b. In boehmite suspensions adsorption of Mn(II) begins at a higher pH than on goethite (7.5 versus 6.5), yet adsorption is complete a full pH unit below the IEP of boehmite. The solubility product of Mn(OH)₂(s) is never exceeded and, as in the case of Mn(II) on goethite, adsorption at all levels has little or no effect on EM.

In Fig. 8 is shown four ESR spectra collected from manganese-containing boehmite suspensions. Spectrum 8a is from a boehmite suspension at high pH in which the Mn(II) was allowed to oxidize, forming a dark-brown precipitate. Spectrum 8b is from a suspension in which full adsorption of the initial $9.04 \times 10^{-5} \text{ M}$ Mn(II) has occurred.

The last two spectra are from suspensions whose initial Mn(II) concentration was $3.61 \times 10^{-4} \text{ M}$ and in which roughly 30% (8c) and 70% (8d) of the Mn(II) initially in solution has adsorbed.

Spectrum 8c shows the characteristic signal for hexaquomanganese(2+) in solution with its six peaks ($\Delta H = 25 \text{ G}$) due to hyperfine splitting. This signal is superimposed on a broader signal ($\Delta H = 190 \text{ G}$). In spectrum 8d the signal due to hexaquomanganese(2+) in solution has greatly diminished in intensity relative to the broader signal. Spectrum 8b, in which no signal for hexaquomanganese(2+) in solution is apparent, corresponds to a suspension in which all Mn(II) has been adsorbed.

The ESR peak intensity is proportional to the magnetic susceptibility of a material provided certain experimental conditions are met (22). These conditions were met for the

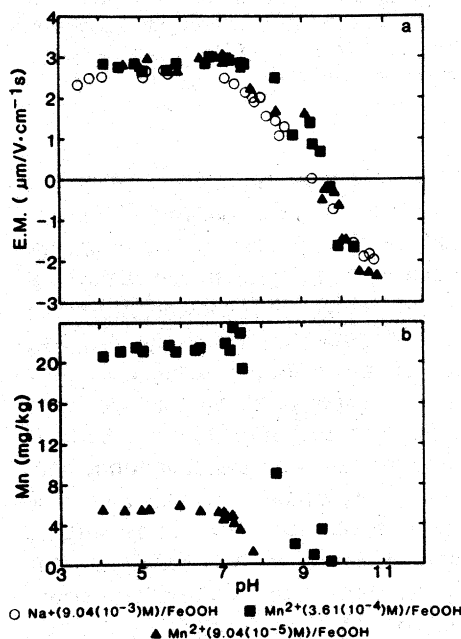


FIG. 6. The variation of the (a) electrophoretic mobility of suspension particles and (b) solution concentration of Mn(II) as a function of pH, for goethite suspensions ($20 \text{ m}^2 \text{ liter}^{-1}$) in $9.04 \times 10^{-3} \text{ M}$ NaClO₄ and two initial concentrations of Mn(ClO₄)₂: 9.04×10^{-5} and $3.61 \times 10^{-4} \text{ M}$.

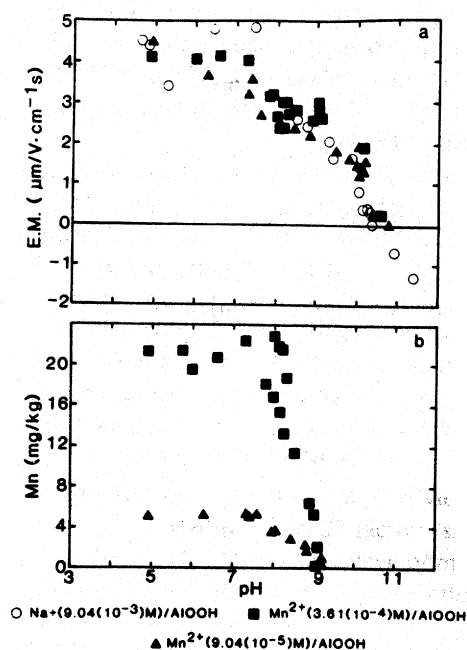


FIG. 7. The variation of the (a) electrophoretic mobility of suspension particles and (b) solution concentration of Mn(II) as a function of pH, for boehmite suspensions ($20 \text{ m}^2 \text{ liter}^{-1}$) in $9.04 \times 10^{-3} \text{ M NaClO}_4$ and two initial concentrations of $\text{Mn}(\text{ClO}_4)_2$: 9.04×10^{-5} and $3.61 \times 10^{-4} \text{ M}$.

spectra we report in this paper. When the inverse of the ESR peak intensity ($1/I$), proportional to the inverse of the magnetic susceptibility ($1/\chi$), is plotted versus the temperature at which the measurement was taken, it is possible to identify the magnetic behavior of the adsorbed manganese. The broad signal of spectra 8b–8d corresponds to an antiferromagnetic material since the ($1/I$) versus temperature plot is a straight line with a positive intercept on the ($1/I$) axis. The correlation coefficient for a least-squares regression of this relation is 0.995 and the origin is not bracketed by the 99.9% confidence interval for the intercept.

In Fig. 9 the temperature dependence of spectrum 8d is revealed. As the temperature was increased up to 100°C the signal due to hexaquomanganese(2+) in solution increased while the broad signal decreased. There was a pronounced, irreversible decrease in the

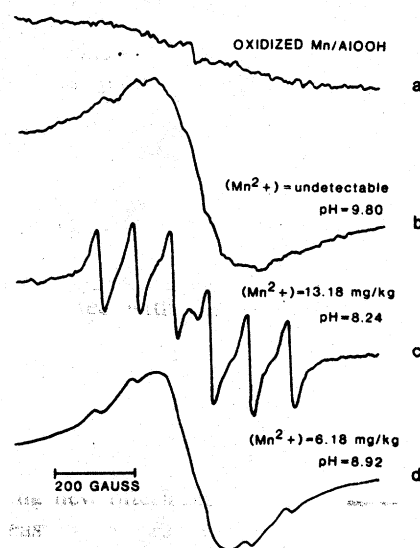


FIG. 8. Electron spin resonance spectra for manganese in selected boehmite suspensions.

intensity of the broad signal above 100°C . There was no moisture loss since the sample was sealed in a capillary tube.

DISCUSSION

The ESR data indicate that Mn(II) on the surface has the properties of an antiferro-

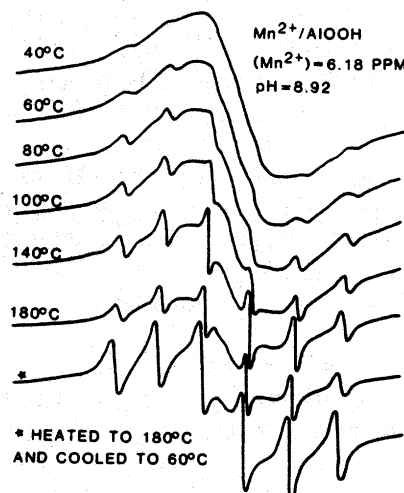


FIG. 9. The temperature dependence of the electron spin resonance spectrum shown in Fig. 8c. There was no moisture loss since the sample was sealed in a capillary tube.

magnetic material, i.e., a material in which the Mn(II) ions form a magnetically ordered lattice with the magnetic dipoles cancelling one another, which solubilizes to hexaquo-manganese(2+) as the temperature is raised, and undergoes an irreversible change above 100°C. The latter two pieces of information suggest the material is a form of hydrous Mn(II) oxide undergoing an irreversible dehydration above 100°C. The material is antiferromagnetic even when the Mn(II) adsorbed is, at most, sufficient for a surface monolayer of close-packed hydrated ions (8b).

Our interpretation is that the Mn(II) on the surface of boehmite has formed Mn(II)-hydroxide clusters that have antiferromagnetic order. The mineral pyrochroite [manganese hydroxide] is antiferromagnetic and the clusters may be structurally similar. If hydroxide clusters form we could explain the insignificant effect of Mn(II) adsorption on suspension EM relatively simply. Mn(II) adsorbed in metal hydroxide clusters would have a much smaller effect on the total particle surface charge, per ion adsorbed, than adsorption as uniformly distributed ions. Furthermore, much of the original boehmite surface would remain exposed. EM measurements would reflect the composite surface charge of two surfaces, Mn(II)-hydroxide clusters and boehmite, with the boehmite surface dominating.

The formation of clusters would minimize the increase in surface energy due to the creation of new interfaces in the system as adsorption proceeds. Of course, this effect must be balanced against the free-energy change associated with the binding of adsorbing ions to surface sites. The formation of metal hydroxide clusters also implies that once certain surface sites have been occupied, further adsorption occurs in association with ions previously adsorbed rather than at other sites on the oxide. Thus, the very process of adsorption creates new adsorption sites that were nonexistent on the "clean" surface.

We observed Mg(II) adsorption below the IEP of goethite. Even though only a small

amount of Mg(II) adsorbs, there is a major effect on the EM of the suspension particles.

This behavior is consistent with adsorption of Mg(II) on sites that are, on the whole, isolated one from another. Since adsorption of such small amounts of Mg(II) [10 to 20% of a monolayer at the IEP] prevents charge reversal, and the pH at which this occurs is well below the pK_1 for hexaquo-magnesium(2+), it is likely that hexaquo-magnesium(2+) is the species adsorbed, at least initially.

On the other hand, boehmite has a high capacity for adsorbing Mg(II). Adsorption begins at a lower pH than on goethite and all of the Mg(II) is eventually adsorbed by pH 10 whereas substantial amounts of Mg(II) remain in solution in goethite suspensions at that pH. The difference in behavior between these two systems occurs despite the fact that they are identical in every way except for the surfaces. In the pH range 10 to 11.5 full adsorption from solution and charge reversal occurs in a boehmite suspension while adsorption has leveled off at much less than a monolayer and charge reversal fails to occur in the goethite suspension. We are forced to attribute these differences to the surfaces and cannot rely on arguments based only on the hydrolytic or solubility properties of Mg(II). The theory of James and Healy (6), as it relates adsorption to the free energy of solvation, fails in this case since the dielectric constant for goethite is larger than for boehmite (cf. (23)). According to this theory the difference in adsorption behavior must be attributed to the only remaining contribution, the adsorption free energy $[\Delta G^\circ_{\text{chem}}]$. James and Healy use this term as an *adjustable* parameter "to obtain a better fit in terms of the amount adsorbed."

We propose that Mg(II) adsorbs as hydroxide clusters on boehmite. We also suggest that Mn(II)-hydroxide clusters form on goethite in view of the minimal effect of adsorbed Mn(II) on the EM of suspension particles. Mg(II) adsorbed on boehmite has a greater effect on the EM of suspension particles than

Mn(II) once full adsorption has occurred (pH range 9.5 to 11.5). This may be due to Mg(II)-hydroxide clusters having a greater positive charge than Mn(II) hydroxide clusters at the same pH.

SUMMARY

Experimentally, we know that Mn(II) adsorbed on boehmite is antiferromagnetic and that adsorption of Mn(II) has an insignificant effect on the EM of both boehmite and goethite suspensions, even when sufficient Mn(II) adsorbs to completely cover the surface four layers thick. From this we conclude that Mn(II) forms hydroxide clusters on boehmite and goethite surfaces, thereby minimizing the effect of adsorption on the EM of suspension particles.

We recorded ESR spectra for goethite suspensions in which adsorption of Mn(II) had occurred, and failed to observe any signal due to Mn(II). Local magnetic fields arising from iron at goethite surfaces may broaden ESR signals of paramagnetic species over distances on the order of 10 Å. If Mn(II)-hydroxide clusters form on goethite surfaces they must be quite small (radius < 10 Å), since the Mn(II) in the cluster must have been subject to this relaxation effect.

The adsorption of Mg(II) on goethite, although limited to a maximum of about 50% of a monolayer, has a dramatic effect on the EM of the suspension particles. We interpret this as arising from the adsorption of Mg(II) as unhydrolyzed hexaquomagnesium(2+) on relatively isolated sites. As for Mg(II) on boehmite, adsorption of sufficient Mg(II) to cover the surface several layers thick has little effect on the EM of suspension particles. By analogy with Mn(II) on goethite and boehmite, we conclude that Mg(II)-hydroxide clusters form on the boehmite surface.

In conclusion we suggest that in addition to the factors generally considered important during adsorption (changes in coulombic and solvation energies, changes in entropy, and site-bond formation) we should consider

two other potentially interrelated factors. First, in addition to the coordination characteristics of individual sites we should perhaps consider the importance of arrangements of groups of sites on the surface and the effect of such arrangements on the cooperative adsorption of species to "nucleate" clusters. Second, balancing the decrease of Gibbs free energy associated with site binding is the increase in free energy associated with the creation of new interfaces in the system due to adsorption. Under certain conditions monolayer adsorption or homogeneous nucleation in solution may be less favorable than cluster formation on the surface from the point of view of creating new interfaces. These factors should at least be considered in the development of theories of ion adsorption from solution.

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